

**2a**, 2 parts recovered *p*-isopropylbenzyloxytriethylsilane, and 48 parts  $\alpha$ -hydroxy- $\alpha$ -triethylsilyl-*p*-isopropyltoluene: nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.96 (s, 4, C<sub>6</sub>H<sub>4</sub>), 5.53 (s, 1, PhCH), 7.17 (septet, 1, *J* = 7 Hz, Me<sub>2</sub>CH), 8.31 (s, 1, OH), 8.76 (d, 6, *J* = 7 Hz, (CH<sub>3</sub>)<sub>2</sub>CH), 8.8–9.6 (m, 15, SiEt<sub>3</sub>).

**Metalation of 2-Trimethylsilyloxypropionitrile (5).** *n*-Butyllithium (23.8 ml, 38.1 mmol) was added to diisopropylamine (3.85 g, 38.1 mmol) in 24 ml of THF at  $-78^\circ$ . **5** (3.62 g, 25.4 mmol) was then added, followed, after 15 min, by triethylchlorosilane (5.7 g, 38.1 mmol). The solution was warmed to  $25^\circ$ . Anhydrous work-up

gave 4.02 g of an oil, containing 62% of 2-trimethylsilyloxy-2-triethylsilylpropionitrile (**7**): bp  $70^\circ$  (0.13 Torr);  $n_D^{30}$  1.5536; ir (neat) 2240 (C $\equiv$ N) and 1250 cm<sup>-1</sup> (Me<sub>3</sub>Si); nmr (CCl<sub>4</sub>, TMS)  $\tau$  8.66 (s, 3, CCH<sub>3</sub>), 7.6–8.9 (m, 15, SiEt<sub>3</sub>), 9.78 (s, 9, OSiMe<sub>3</sub>).

*Anal.* Calcd for C<sub>12</sub>H<sub>27</sub>NOSi<sub>2</sub>: C, 56.50; H, 10.67; Si, 22.00. Found: C, 57.08; H, 10.69; Si, 21.28.

Repeating the reaction, derivatizing with trimethylchlorosilane gave 15% 2-trimethylsilyloxy-2-trimethylsilylpropionitrile (**6**): ir (neat) 2230 (C $\equiv$ N) and 1250 cm<sup>-1</sup> (Me<sub>3</sub>Si); nmr (CCl<sub>4</sub>, TMS)  $\tau$  8.65 (s, 3, CCH<sub>3</sub>), 9.78 (s, 9, OSiMe<sub>3</sub>), 9.84 (s, 9, SiMe<sub>3</sub>).

## New Anionic Rearrangements. XVIII. 1,2-Anionic Rearrangements from Sulfur to Carbon in Benzylthiotrimethylsilane and Benzylthiotrimethylgermane<sup>1,2</sup>

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**Abstract:** Benzylthiotrimethylsilane (**1a**) and benzylthiotrimethylgermane (**1b**), upon metalation at the benzyl carbon atom with excess *tert*-butyllithium or lithium diisopropylamide in tetrahydrofuran, rearrange rapidly *via* 1,2-shift of silicon or germanium to the  $\alpha$  carbanion to give, in high yield, anions of  $\alpha$ -mercapto- $\alpha$ -trimethylsilyltoluene (**2a**) and  $\alpha$ -mercapto- $\alpha$ -trimethylgermyltoluene (**2b**), respectively. These anions can be protonated, alkylated, or silylated at sulfur. **2a** and **2b** rearrange spontaneously at  $195^\circ$ , or at  $100^\circ$  in the presence of catalytic amounts of radical initiator, to **1a** and **1b**, respectively, in high yield. In this novel catalytic rearrangement, the neutral species **1a** and **1b** are thermodynamically favored over **2a** and **2b**. In the anion rearrangement, the equilibrium is between anions, and the stability gained by placing the negative charge on sulfur, rather than on carbon, makes the anions of **2a** and **2b** the favored isomers at equilibrium. Methylthio-*tert*-butyldimethylsilane, upon metalation, rearranges to *tert*-butyldimethylsilylmethanethiol.

In the previous paper we reported that benzyloxytrimethylsilane, upon metalation at the benzyl carbon atom with excess *tert*-butyllithium, rearranges rapidly and in high yield *via* 1,2-shift of silicon from oxygen to the  $\alpha$  carbanion to give the anion of  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**1c'**  $\rightarrow$  **2c'**, Scheme I). The analogous germanium rearrangement, **1d'**  $\rightarrow$  **2d'**, was also described.

In searching for new examples of 1,2-anionic silicon and germanium rearrangements, the sulfur analogs of **1c** and **1d**, benzylthiotrimethylsilane (**1a**) and benzylthiotrimethylgermane (**1b**), were considered. If these molecules could be selectively metalated at the benzyl carbon atoms, migration of silicon or germanium from sulfur to the  $\alpha$  carbanion might occur. The weak silicon-sulfur bond in **1a'**, and the weakly basic sulfur anion in **2a'**, could be expected to make the isomerization **1a'**  $\rightarrow$  **2a'** even more thermodynamically favored than the analogous isomerization of the oxygen species **1c'**  $\rightarrow$  **2c'**.

The counterpart to the alkoxy silane to silylcarbinol rearrangement **1c'**  $\rightarrow$  **2c'** in organic chemistry is the well known Wittig rearrangement of a metalated ether to its isomeric alcohol.<sup>4,5</sup> As discussed previously,<sup>2</sup>

migration of carbon from oxygen to the carbanion is slow.<sup>6</sup> When silicon migrates, rearrangement can be fast, because silicon may become pentacoordinate in the transition state,<sup>7</sup> removing the symmetry restrictions<sup>8</sup> to rearrangement present in the Wittig rearrangement.<sup>9</sup>

The counterpart to the silicon-sulfur rearrangement **1a'**  $\rightarrow$  **2a'** in organic chemistry would be the isomerization of a metalated organic sulfide to a mercaptide anion, in which migration of carbon from sulfur to an  $\alpha$  carbanion would occur. This process is not observed; metalation of the rather acidic proton  $\alpha$  to sulfur in sulfides,<sup>10</sup> sulfoxides,<sup>16</sup> and sulfones<sup>17</sup> commonly pro-

(5) D. L. Dalrymple, T. L. Kruger, and W. N. White in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967, p 617.

(6) H. Schäfer, U. Schöllkopf, and D. Walter, *Tetrahedron Lett.*, 2809 (1968).

(7) A. G. Brooke, G. E. Legrow, and D. M. MacRae, *Can. J. Chem.*, 45, 239 (1967).

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(9) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, 9, 763 (1970).

(10) For example: CH<sub>3</sub>SCH<sub>2</sub>Li,<sup>11,12</sup> PhSCH<sub>2</sub>Li,<sup>14</sup> lithiated 1,3-dithianes.<sup>15</sup>

(11) D. J. Peterson, *J. Org. Chem.*, 32, 1717 (1967).

(12) But note that CH<sub>3</sub>OCH<sub>2</sub>Li appears under Wittig rearrangement to LiOCH<sub>2</sub>CH<sub>3</sub>.<sup>13</sup>

(13) U. Schöllkopf and H. Kuppers, *Tetrahedron Lett.*, 1503 (1964).

(14) H. Gilman and F. J. Webb, *J. Amer. Chem. Soc.*, 71, 4062 (1949).

(15) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 4, 1075 (1965).

(16) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 87, 1345 (1965).

(17) B. S. Thyagarajan, *Mech. React. Sulfur Compounds*, 4, 115 (1969).

(1) This work was supported in part by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR 70-1904.

(2) Previous paper in this series: A. Wright and R. West, *J. Amer. Chem. Soc.*, 96, 3214 (1974).

(3) Procter and Gamble Fellow, 1972–1973.

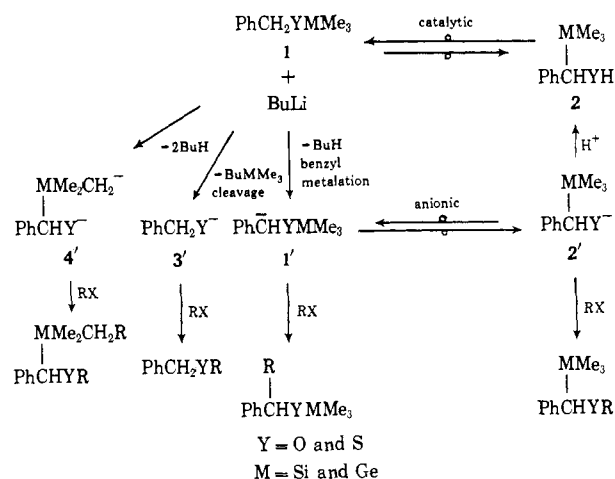
(4) G. Wittig and L. Löhmann, *Justus Liebigs Ann. Chem.*, 550, 260 (1942).

duces stable carbanions which do not rearrange.<sup>18-24</sup> However, anions of **1a** and **1b** do rearrange<sup>26</sup> to anions of  $\alpha$ -mercapto- $\alpha$ -trimethylsilyltoluene (**2a**) and  $\alpha$ -mercapto- $\alpha$ -trimethylgermyltoluene (**2b**), respectively. These are apparently the first examples of Wittig-type [1,2]-sigmatropic shifts involving migration of an atom from sulfur to negatively charged carbon. We also report novel radical and thermal rearrangements that allow **2a** and **2b** to be rapidly isomerized back to **1a** and **1b**, respectively.

### Metalations

Metalation of the compounds listed in Table I occurs as outlined in Scheme I. Products are identified

Scheme I



throughout this paper systematically by a number (for structure type), a prime (if an anion), a letter (to identify substituents, as listed in Table I), and the identity of derivative groups if other than H. Thus, for example, the methyl derivative of anion **1a'** is **1a** (R = CH<sub>3</sub>).

The distribution of anions resulting from metalation of substrates is inferred from the compositions of solutions resulting from quenching the anions with protonating, alkylating, or silylating agents. Table I shows the amounts of each derivative isolated, listed under the species in the anion solution from which it is believed to be derived. Percentages are based on the total of all species originating from **1** appearing in solution. The data in Table I are for metalation in tetrahydrofuran (THF) at  $-78^\circ$  using *tert*-butyllithium as base.

Metalation of **1a** and **1b** at the benzyl carbon atom apparently occurs faster than metalation of the oxygen

(18) A Wittig-like mechanism has been used to explain the formation of stilbene from benzyl sulfide and strong base.<sup>19</sup>

(19) T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965).

(20) The remote rearrangement  $\text{LiC}_6\text{H}_4\text{SSiMe}_3 \rightarrow \text{Me}_3\text{SiC}_6\text{H}_4\text{SLi}$  has been reported.<sup>21</sup>

(21) A. R. Basindale and D. M. R. Walton, *J. Organometal. Chem.*, **25**, 389 (1970).

(22) Recently, products possibly arising from [1,2]-sigmatropic shifts have been isolated upon metalation of alkylbenzyl sulfides, despite failure of earlier workers to isolate such products:<sup>23</sup> J. F. Biellman, private communication.

(23) C. R. Hauser, S. W. Kantor, and W. R. Braun, *J. Amer. Chem. Soc.*, **75**, 2660 (1953).

(24) Metalated bis allyl sulfides readily undergo a symmetry-allowed [2,3]-sigmatropic shift at  $-78^\circ$ .<sup>25</sup>

(25) J. F. Biellman and J. B. Ducep, *Tetrahedron Lett.*, 33 (1971).

(26) A brief account of some of this work has appeared; see A. Wright, D. Ling, P. Boudjouk, and R. West, *J. Amer. Chem. Soc.*, **94**, 4784 (1972).

Table I. Anionic Rearrangements<sup>a</sup>

Substrate	Y	M	R-X	Yields of anion derivatives, <sup>b</sup> %				
				1	1'	2'	3'	4'
<b>1a</b>	S	Si	H-OH	0	0	90	0	10
			Et <sub>3</sub> Si-Cl	0	0	90	0	10
			CH <sub>3</sub> -I	0	0	86	2	12
			CH <sub>3</sub> -SO <sub>2</sub> CH <sub>3</sub>	0	0	87	3	11
<b>1b</b>	S	Ge	H-OH	0	0	75	25	0
			Et <sub>3</sub> Si-Cl	0	0	72	28	0
			CH <sub>3</sub> -I	0	0	74	27	0

<sup>a</sup> Metalations conducted in THF at  $-78^\circ$  using *tert*-butyllithium. Time of metalation, hr: **1a**, 0.01; **1b**, 0.80. <sup>b</sup> The derivative is listed under the species in the anion solution from which it is believed to be derived.

analogs **1c** and **1d**. A time of only 30 sec is required for the complete metalation of **1a** under the above conditions but over 2 min are required for the metalation of **1c**. More astonishing results are obtained using lithium diisopropylamide as base. Under these conditions **1c** is metalated in good yield only after 12 hr at  $25^\circ$ , whereas **1a** is metalated at the benzyl position in 85% yield after only 5 min at  $0^\circ$ . Actually, it is well known that sulfur,<sup>10</sup> but not oxygen,<sup>27</sup> has an acidifying influence on proton bearing  $\alpha$ -carbon atoms. This may be due to the larger size of and the availability of 3d orbitals on the sulfur atom.

Other reactions occur between the metalation reagent and **1** in addition to benzyl metalation. One such side reaction is the cleavage of the silicon-sulfur or germanium-sulfur bond by the metalating reagent<sup>28,29</sup> (**1**  $\rightarrow$  **3'**). Results in Table I show the germanium species **1b** is more susceptible to such cleavage than the silicon analog **1a**. Cleavage is no more important for the sulfur compounds **1a** and **1b** than for the oxygen compounds **1c** and **1d**. One might have expected, because of the weak silicon-sulfur bond, that more **3a'** than **3c'** should have appeared in solution. However, **1a** is consumed faster than **1c** in the formation of **2'**, so that even if **1a** is cleaved to **3a'** faster than **1c** is to **3c'**, less of **1a** is available for such cleavage. When *n*-butyllithium was used only cleavage occurred regardless of substrate. Lithium diisopropylamide produced little cleavage in **1a**.

The second side reaction involves metalation of the slightly acidic methyl groups attached to silicon (**1**  $\rightarrow$  **4'**).<sup>30</sup> As is characteristic of germanium compounds, germymethyl metalation does not occur.<sup>31</sup> Lithium diisopropylamide is an insufficiently strong base to cause silylmethyl metalation. However, when *tert*-butyllithium is used for metalation of **1a**, the resulting anion solution shows in its pmr spectrum a resonance at  $\tau$  12.15, characteristic of the SiCH<sub>2</sub>Li species.<sup>30</sup> Upon quenching this anion solution with methyl iodide, about 12%  $\alpha$ -methylthio- $\alpha$ -dimethylethylsilyltoluene (**4a**, R = CH<sub>3</sub>) is isolated. The dianion from which this derivative is produced, PhCH(SLi)SiMe<sub>2</sub>CH<sub>2</sub>Li, apparently arises from methyl metalation of **1a**, not **2a'**,

(27) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969).

(28) R. West and G. A. Gornowicz, *J. Organometal. Chem.*, **28**, 25 (1971).

(29) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 12 and 13.

(30) J. W. Connally and G. Urry, *Inorg. Chem.*, **2**, 645 (1963); D. J. Peterson, *J. Organometal. Chem.*, **1**, 373 (1967); G. E. Hartwell and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4625 (1966).

(31) F. Glockling, "The Chemistry of Germanium," Academic Press, London, England, 1969, Chapter 1.

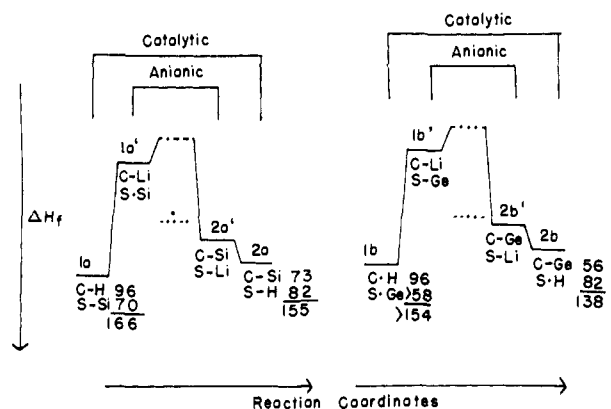


Figure 1. Energy diagrams for the interconversions of isomers of compounds of the class  $\text{PhCH}_2\text{YMMe}_3$  (**1**) and  $\text{PhCHYMMe}_3$  (**1'**). Approximate thermochemical bond energies are calculated from heats of combustion of simple model compounds:  $E(\text{C}-\text{H})\text{CH}_4$  and  $E(\text{S}-\text{H})\text{H}_2\text{S}$  from J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968;  $E(\text{Si}-\text{C})\text{Me}_3\text{SiC}$  and  $E(\text{Ge}-\text{C})\text{Et}_4\text{Ge}$  from E. A. V. Ebsworth in "Organometallic Compounds of Group IV Elements," A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 46;  $E(\text{Si}-\text{S})\text{SiS}_2$  from T. L. Cottrell, "Strengths of Chemical Bonds," 2nd ed., Butterworths, London, 1958;  $E(\text{Ge}-\text{S})$ , see text. Similar data for the oxygen analogs are given in Figure 1 of the preceding paper, ref 2.

since yields of the dianion are high if the *tert*-butyllithium is added at  $-20^\circ$  instead of  $-78^\circ$  but low if the preferred anion solution, **2a'**, is warmed to  $25^\circ$  in the presence of excess *tert*-butyllithium solution. In the metalation of **1c**, the silylmethyl metalated product is the monoanion  $\text{PhCH}_2\text{OMe}_2\text{CH}_2\text{Li}$ , which apparently cannot be subsequently metalated at the benzylic position.

### Anion Rearrangements

Aqueous quenching of **1a** 30 sec after metalation with excess *tert*-butyllithium at  $-78^\circ$  yields **2a** as the only isolated product of reaction. The absence of **1a** or its hydrolysis product, benzyl mercaptan, as a product indicates that the metalation of **1a** to form **1a'** is complete within 30 sec and that rapid isomerization of **1a'** to **2a'** follows. This represents the first example of a Wittig-like migration of silicon from sulfur to an  $\alpha$  carbanion. Being fast and selective, the rearrangement is an excellent method for synthesizing mercaptoorganosilanes. Lithium diisopropylamide, a reagent which is cheaper and easier to handle than *tert*-butyllithium, may be used as the metalating agent with excellent results.

The anions prepared from **1a** and **2a** in THF have identical pmr spectra; there is only one trimethylsilyl resonance at  $\tau$  6.90, due to the one remaining benzylic proton, and a multiplet at  $\tau$  2.50–3.50, due to the five phenyl protons. In pentane, the resonance due to the phenyl protons of the anion consists of a sharp singlet at  $\tau$  2.86. As discussed previously,<sup>2</sup> if the anion were of the form **1a'**, there should be a considerable upfield shift in the phenyl proton resonances due to delocalization of charge into the ring from the benzylic carbanion.<sup>32</sup> There is no upfield shift in pentane. The multiplet in THF is probably due to restricted motion of the phenyl group, not charge delocalization, since

(32) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963).

there is little or no net upfield shift. The anion was stable even when heated briefly to  $180^\circ$ . This stability would be expected of the form **2a'** but not of **1a'**.

The anion solution prepared from **1a** and *tert*-butyllithium is red, whereas that from **1a** and lithium diisopropylamide is colorless. Since the two solutions appear almost chemically identical, the color in the former is probably due to unidentified minor metalation products.

Triethylchlorosilane, methyl iodide, and methyl sulfate all give derivatives of the rearranged form **2a'** only. If **1a'** and **2a'** were in rapid equilibrium with each other, with **1a'** comprising a significant fraction of the anion solution, it would still be possible for derivatives of **2a'** alone to form, provided the quenching agents reacted much faster with **2a'** than **1a'**. Since it is unlikely that all three quenching agents would react with **2a'** much faster than with **1a'**, it is probable that there is little, if any, **1a'** present in the anion solution. The germanium species **1b** behaves in exactly the same fashion as **1a**. The form **2b'** appears to be the only isomer present in solution.

### Catalytic Silicon Rearrangements

The fact that the anion **2a'** is thermodynamically favored over the anion **1a'** in solution gives no indication as to which of the neutral species **1a** or **2a** would be thermodynamically preferred if a kinetic pathway were available for their equilibration with each other. In the analogous oxygen system, whereas **2c'** is more stable than **1c'** in solution, it is possible to isomerize **2c** to **1c** using catalytic amounts of a base<sup>33,34</sup> such as triethylamine,<sup>35</sup> liquid sodium-potassium alloy, or even the lithium alkoxide **2c'**.<sup>2</sup>

The relationships between the anionic and catalytic rearrangements for the systems **1a** and **1b** are shown in Figure 1. The relative heats of formation of the species involved are diagrammed qualitatively, consistent both with the experimental results to be described and with the known approximate thermochemical bond energies of the bonds made and broken in the isomerizations. For the silyl-sulfur system of **1a**, Figure 1 shows that the sum of the Si-S and C-H bond energies exceeds the sum of the Si-C and S-H bond energies, so that **1a** should be thermodynamically preferred over **2a** as is **1c** over **2c** in the oxygen system. Thus, **2a** should rearrange to **1a** catalytically.

To test this prediction, it was necessary to find an effective catalyst for the equilibration of **1a** and **2a**. No catalytic rearrangement of an  $\alpha$ -silyl mercaptan to an alkylthiosilane has been reported. The favored catalyst for the Brook rearrangement, liquid sodium-potassium alloy, does not isomerize **2a** to **1a**. Instead, **2a'** is formed with liberation of hydrogen. **2a'** does not catalyze the conversion of **2a** to **1a** even at elevated temperatures. We have, however, discovered a catalyst which does isomerize **2a** to **1a**, vindicating our prediction, and providing the first example of a 1,2-migration of a silicon or germanium atom from carbon to sulfur.

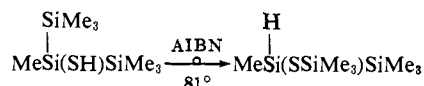
Pitt has reported the radical-catalyzed quantitative

(33) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Amer. Chem. Soc.*, **81**, 981 (1959); G. J. P. Peddle and J. E. H. Ward, *J. Organometal. Chem.*, **13**, 269 (1968).

(34) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

(35) M. S. Biernbaum and H. S. Mosher, *J. Amer. Chem. Soc.*, **93**, 6221 (1971).

1,2-migration of the trimethylsilyl group from silicon to sulfur in isomerizations of mercaptopolysilanes.<sup>36</sup>



Heating **2a** in heptane for 37 min at 100° in the presence of a catalytic amount of azoisobutyronitrile (AIBN), the catalyst used by Pitt, gives 92% **1a** and 8% recovered **2a**. Negligible rearrangement of **2a** to **1a** occurs in the absence of radical initiator in 10 min at 100° or in the presence of the nonradical products of previously decomposed initiator.

When **2a** was heated to 195°, however, quantitative first-order thermal rearrangement to **1a** does occur ( $k = 0.97 \times 10^{-3} \text{ sec}^{-1}$ ). In contrast silylcarbinol **2c** rearranges to **1c** only at 275° and then only slowly with formation of several side products. The thermal isomerization of **2a** to **1a** is not accelerated in the presence of a polar solvent, such as benzonitrile, suggesting that the transition state is nonpolar. Rearrangement probably occurs through catalysis by thermally generated thio radicals. Thus **1a**, not **2a**, is actually the thermodynamically preferred species at equilibrium, and the failure of the base-catalyzed rearrangement of **2a** to **1a** must be attributed to kinetic factors. Indeed, the thermal rearrangement of **2a** to **1a** is accelerated only slightly at 195° in the presence of a small amount of **2a'**. As can be seen from the qualitative energy diagram in Figure 1, **2a'**, because of the low basicity of the sulfide anion, may have an energy too far below the transition state to be an effective catalyst.

### Catalytic Germanium Rearrangements

Although  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**2c**) undergoes the base-catalyzed Brook rearrangement to form **1c**,  $\alpha$ -hydroxy- $\alpha$ -trimethylgermyltoluene (**2d**) does not isomerize. There is evidence that the absence of rearrangement is due to an inaccessible transition state and perhaps also to **2d** being thermodynamically preferred to **1d**.

It was therefore of interest to see if  $\alpha$ -mercapto- $\alpha$ -trimethylgermyltoluene (**2b**) could be catalytically isomerized to **1b**. The isomerization requires that the sum of the Ge-S and C-H bond energies be greater than the sum of the C-Ge and SH bond energies (Figure 1). Apparently no direct determination of the Ge-S bond strength has been made, but it is known that trimethylsilylethanethiolate exists in the form  $\text{CH}_3\text{C}(\text{=S})\text{OSiMe}_3$ , not  $\text{CH}_3\text{C}(\text{=O})\text{SSiMe}_3$ ,<sup>37</sup> showing that the Si-O bond is at least approximately 15 kcal/mol stronger than the Si-S bond. We have synthesized trimethylgermylethanethiolate<sup>38</sup> and observed a very strong C=O stretch at 1680  $\text{cm}^{-1}$ , showing that the molecule assumes the form  $\text{CH}_3\text{C}(\text{=O})\text{SGeMe}_3$  and consequently that the Ge-O bond is not more than approximately 15 kcal stronger than the Ge-S bond. Since the Ge-O bond is reported to be 73 kcal/mol, the minimum strength of the Ge-S bond is about 58 kcal/

mol, still sufficient to make **1b** the stable species at equilibrium.

In fact heating **2b** to 100° for 10 min in heptane in the presence of a catalytic amount of AIBN gives 96% conversion to **1b**. Negligible rearrangement of **2b** to **1b** occurs in the absence of radical initiator in 10 min. When **2b** was heated to 195°, however, thermal rearrangement to **1b** occurred,  $k = 3.62 \times 10^{-3} \text{ sec}^{-1}$ . The rate of rearrangement is 3.7 times greater than that of mercaptosilane **2a**. Like **2a**, **2b** forms **2b'** with sodium-potassium alloy, without isomerization to **1b** occurring.

Table II summarizes the attempted catalytic isomeri-

Table II. Catalytic Rearrangements (Conversions, %)

PhC(MMe <sub>3</sub> )HYH ↔ PhCH <sub>2</sub> YMMe <sub>3</sub>	M, Y			
	Si, O	Si, S	Ge, O	Ge, S
0.08 equiv of AIBN, 100°	0	92	0	96
Neat, 195°	0	98	0	86
Na-K, 25°	92	0	0	0
0.10 equiv of <i>n</i> -BuLi, 25°	86	0	0	0

zation of **2a**, **2b**, **2c**, and **2d**. The extreme difference in behavior between **2c** and **2d** is interesting in light of the similar rates of isomerization of **2a** and **2b**. It would seem, from these data, that the absence of the catalytic rearrangement of **2d** is related to the strengths of the bonds made and broken, not to a basic reluctance of germanium, compared to silicon, to undergo 1,2-rearrangements.

### Anion Rearrangement of Methylthio-*tert*-butyldimethylsilane

It is known that sulfur acidifies protons at the  $\alpha$ -carbon atom in alkyl sulfides.<sup>10</sup> Thus metalation of compounds such as methylthiotrimethylsilane at the sulfur methyl position should be possible. Unfortunately, it has been reported that methoxytrimethylsilane is completely cleaved by *tert*-butyllithium<sup>26</sup> to produce lithium methoxide and *tert*-butyltrimethylsilane. In order to prevent a similar cleavage of the sulfur-silicon bond, the substrate methylthiodimethyl-*tert*-butylsilane (**5**) was chosen for study.



**5**, treated with *tert*-butyllithium in THF, followed by quenching with aqueous acid, yields 35% dimethyl-*tert*-butylsilylmethanethiol (**6**) and 65% recovered **5**. Thus a sulfur to carbon migration of silicon has occurred in a system not containing a phenyl group. Metalating at 25° with *tert*-butyllithium TMEDA complex gives 32% **6** and several side products.

### Experimental Section

All reactions involving organolithium compounds were carried out in an atmosphere of dry nitrogen. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were recorded on Varian A-60 and JEOL MH-100 spectrometers. Gas-liquid chromatographic (glc) separations were made on a Varian Aerograph A-700 chromatograph using columns packed with either SE-30 or QF-1 silicone on Chromosorb W. Mass spectra were obtained using an AEI Model MS-9 spectrometer. All boiling points and melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-33 spectrometer.

Reaction product mixtures were purified by distillation and then

(36) C. G. Pitt and M. S. Fowler, *J. Amer. Chem. Soc.*, **90**, 1928 (1968).

(37) G. A. Gornowicz and J. W. Ryan, *J. Org. Chem.*, **31**, 3439 (1966).

(38) Triphenylgermylethanethiolate is known, but its ir spectrum is not reported; see W. E. Davidson, K. Hills, and M. C. Henry, *J. Organometal. Chem.*, **3**, 285 (1965).

resolved into individual pure compounds by preparative glc. Reported product distributions are based on relative glc peak areas confirmed, where possible, by nmr analysis of crude reaction mixtures. Unless otherwise noted, distillations were completed with less than ca. 5% residue remaining in the stillpot.

*tert*-Butyllithium, 1.27 *M* in pentane, and *n*-butyllithium, 1.6 *M* in hexane, were obtained inexpensively in 1-gallon cylinders from Foote Mineral Co., New Johnsonville, Tenn. Tetrahydrofuran (THF) was dried by distillation from LiAlH<sub>4</sub> just prior to use.

All other reagents were either prepared by distillation procedures or obtained from commercial sources and purified prior to use if necessary.

**Benzylthiotrimethylsilane (1a).**  $\alpha$ -Mercaptotoluene (124 g, 1 mol) was added to 194 g (1.2 mol) of hexamethyldisilazane in 300 ml of toluene and the solution gently refluxed for 72 hr. Glc analysis showed 100% silylation. Anhydrous work-up gave 169 g (86%) of **1a**: bp 80° (1.6 Torr);  $n_D^{20}$  1.5305;  $d_4^{20}$  = 0.966; ir (neat) 1250 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>)  $\tau$  2.79 (s, 5, Ph), 6.35 (s, 2, CH<sub>2</sub>); 9.79 (s, 9, SiMe<sub>3</sub>).

*Anal.* Calcd for C<sub>16</sub>H<sub>18</sub>SSi: C, 61.20; H, 8.21; Si, 14.26; S, 16.30. Found: C, 61.34; H, 8.24; Si, 13.84; S, 16.48.

**Benzylthiotrimethylgermane (1b).** Triethylamine (5.2 g, 50 mmol) was added to a solution of 6.4 g (50 mmol) of  $\alpha$ -mercaptotoluene and 7.8 g (50 mmol) of trimethylchlorogermane<sup>2</sup> in 50 ml of toluene and the resulting mixture heated briefly to 100°. Filtration followed by anhydrous work-up gave 9.8 g (80%) of **1b**: bp 85° (0.12 Torr);  $n_D^{20}$  1.5536; nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.80 (s, 5, Ph), 6.35 (s, 2, CH<sub>2</sub>), 9.64 (s, 9, GeMe<sub>3</sub>).

*Anal.* Calcd for C<sub>10</sub>H<sub>16</sub>GeS: C, 49.86; H, 6.69; S, 13.31. Found: C, 50.42; H, 6.64; S, 13.22.

**Methylthiodimethyl-*tert*-butylsilane (5).** *n*-Butyllithium (17.1 cm<sup>3</sup>, 27.3 mmol, 1.6 *M*) was added to a solution of 1.3 g (27.3 mmol) of methanethiol and 4.1 g (27.3 mmol) of *tert*-butyldimethylchlorosilane in 25 ml of ether. After refluxing 24 hr distillation gave 4.0 g (91%) of **5**: bp 170° (760 Torr);  $n_D^{20}$  1.4673; ir (neat) 1250 cm<sup>-1</sup> (SiMe<sub>2</sub>); nmr (CCl<sub>4</sub>, TMS)  $\tau$  8.10 (s, 3, SCH<sub>3</sub>), 8.95 (s, 9, Si-*t*-Bu), 9.75 (s, 6, SiMe<sub>2</sub>).

*Anal.* Calcd for C<sub>7</sub>H<sub>8</sub>SSi: C, 51.8; H, 11.2; S, 19.8. Found: C, 52.23; H, 11.42; S, 19.17.

**Anionic Rearrangements.** The time and temperatures for each metalation are listed in Table I. For all metalations in which the same solvent system was used, the same procedure was followed, as illustrated below. Unless otherwise stated, trivial products were identified by their nmr spectra or by comparison of retention times with an authentic specimen on both SE-30 and QF-1 glc columns.

**Rearrangement of Benzylthiotrimethylsilane 1a.** *tert*-Butyllithium (266 ml, 0.33 mol) was added to **1a** (59 g, 0.30 mol) in 266 ml of THF at -78°. The pmr spectrum of the anion solution showed a trimethylsilyl resonance at  $\tau$  10.07 and a SiCH<sub>2</sub>Li resonance at  $\tau$  12.15. The anion solution was divided into four portions of 150 ml each. To the first was added 2.2 *M* MgCl<sub>2</sub> solution at -78°. Work-up gave 12.7 g (85%) of  $\alpha$ -mercapto- $\alpha$ -trimethylsilyltoluene (**2a**): bp 79° (0.135 Torr);  $n_D^{20}$  1.5393; ir (neat) 2570 cm<sup>-1</sup> (SH); nmr (CCl<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>)  $\tau$  2.86 (s, 5, Ph), 6.73 (d, 1, CHSH, *J* = 7 Hz), 8.38 (d, 1, CHSH, *J* = 7 Hz), 9.96 (s, 9, SiMe<sub>3</sub>).

*Anal.* Calcd for C<sub>10</sub>H<sub>16</sub>SSi: C, 61.8; H, 9.75; S, 10.30; Si, 18.11. Found: C, 62.19; H, 9.43; S, 10.41; Si, 18.01.

To the second 150-ml portion of anion was added 10.6 g (75 mmol) of CH<sub>3</sub>I. A heavy white precipitate formed immediately. Anhydrous work-up gave 13.4 g (89%) of an oil consisting of 2 parts benzylmethyl sulfide, identified from the pmr spectrum of the isolated compound, and 86 parts  $\alpha$ -methylthio- $\alpha$ -trimethylsilyltoluene (**2a**, R' = CH<sub>3</sub>):  $n_D^{20}$  1.5284; ir (neat) 1250 cm<sup>-1</sup> (MeSi); nmr (CCl<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>)  $\tau$  2.80 (s, 5, Ph), 6.91 (s, 1, PhCH), 8.15 (s, 3, CH<sub>3</sub>), 9.98 (s, 9, SiMe<sub>3</sub>).

*Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>SSi: C, 62.70; H, 8.61; S, 15.22; Si, 13.34. Found: C, 62.79; H, 8.67; S, 15.18; Si, 13.12.

Also isolated were 12 parts  $\alpha$ -methylthio- $\alpha$ -dimethylethylsilyltoluene:  $n_D^{20}$  1.5348; ir (neat) 1250 cm<sup>-1</sup> (Me<sub>2</sub>Si); nmr (CCl<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>)  $\tau$  2.97 (s, 5, Ph), 6.90 (s, 1, PhCH), 8.17 (s, 3, CH<sub>3</sub>), 8.92-9.15 (m, 5, SiEt), 9.99 (s, 3, SiMe), 10.05 (s, 3, SiMe).

*Anal.* Calcd for C<sub>12</sub>H<sub>20</sub>SSi: C, 64.22; H, 8.98; S, 14.28; Si, 12.51. Found: C, 64.38; H, 9.04; S, 13.96; Si, 12.70.

To the third 150-ml portion was added 9.5 g (75 mmol) of Me<sub>2</sub>SO<sub>4</sub>. Anhydrous work-up gave 13.1 g (87%) of an oil consisting of 3 parts benzylmethyl sulfide, 87 parts **2a** (R' = CH<sub>3</sub>), and 11 parts  $\alpha$ -methylthio- $\alpha$ -dimethylethylsilyltoluene.

To the fourth 150-ml portion was added 11.3 g (75 mmol) of Et<sub>3</sub>SiCl. Reaction occurred slowly at 25° to give, upon anhydrous work-up, 20 g (80%) of an oil consisting of two compounds, present

in the ratio 9:1, according to analytical glc. The more abundant compound was isolated and found to be  $\alpha$ -triethylsilylthio- $\alpha$ -trimethylsilyltoluene (**2a**, R' = Et<sub>3</sub>Si): bp 122° (0.140 Torr); ir (neat) 1250 cm<sup>-1</sup> (SiMe<sub>3</sub>); nmr (CCl<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>)  $\tau$  2.85 (s, 5, Ph), 6.95 (s, 1, PhCH), 8.9-9.6 (m, 15, SiEt<sub>3</sub>), 9.98 (s, 9, SiMe<sub>3</sub>).

*Anal.* Calcd for C<sub>16</sub>H<sub>31</sub>SSi<sub>3</sub>: C, 61.80; H, 9.75; S, 10.31; Si, 18.14. Found: C, 62.19; H, 9.43; S, 10.41; Si, 18.01.

Hydrolysis of **2a** (R' = Et<sub>3</sub>Si) by stirring with water for 16 hr gave triethylsilanol, hexaethyldisiloxane, and **2a**, confirming the proposed structure.

The less abundant compound was of too high a molecular weight to be isolated by preparative glc. The nmr spectrum of the unresolved oil showed a resonance at  $\tau$  10.22, typical of the Si<sub>2</sub>CH<sub>2</sub> moiety, and suggested the compound was PhCH(SSiEt<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>-SiEt<sub>3</sub>.

**Rearrangement of Benzylthiotrimethylgermane 1b.** **1b** was metalated and derivatized exactly as was **1a**. CH<sub>3</sub>I quenching gave 27 parts benzyl methyl sulfide and 74 parts  $\alpha$ -methylthio- $\alpha$ -trimethylgermyltoluene (**2b**, R' = CH<sub>3</sub>):  $n_D^{20}$  1.5468; nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.79 (s, 5, Ph), 6.72 (s, 1, PhCH), 8.12 (s, 3, SCH<sub>3</sub>), 9.84 (s, 9, GeMe<sub>3</sub>).

*Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>GeS: C, 51.80; H, 7.12; S, 12.56. Found: C, 51.70; H, 7.11; S, 12.62.

Quenching with triethylchlorosilane occurred slowly at 25° and gave two compounds in the ratio 28:72. The first was  $\alpha$ -triethylsilylthio- $\alpha$ -triethylsilyltoluene, an unusual product resulting probably from successive metalations and silylations of  $\alpha$ -mercaptotoluene: nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.78 (s, 5, Ph), 6.85 (s, 1, PhCH), 8.9-9.6 (m, 30, 2SiEt<sub>3</sub>).

*Anal.* Calcd for C<sub>19</sub>H<sub>36</sub>SSi<sub>3</sub>: C, 64.72; H, 10.28; S, 9.08. Found: C, 65.16; H, 10.21; S, 8.72.

The second product was  $\alpha$ -triethylsilylthio- $\alpha$ -trimethylgermyltoluene (**2b**, R' = SiEt<sub>3</sub>):  $n_D^{20}$  1.5318; nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.76 (s, 5, Ph), 6.72 (s, 1, PhCH), 9.0-9.6 (m, 15, SiEt<sub>3</sub>), 9.82 (s, 9, GeMe<sub>3</sub>).

*Anal.* Calcd for C<sub>18</sub>H<sub>30</sub>GeSSi: C, 54.2; H, 8.50; S, 9.03. Found: C, 54.75; H, 8.25; S, 9.18.

Hydrolysis in basic H<sub>2</sub>O-THF solution gave  $\alpha$ -mercapto- $\alpha$ -trimethylgermyltoluene (**2b**), 90% pure, but too heat sensitive for further purification by preparative glc: ir (neat) 2560 cm<sup>-1</sup> (SH); nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.95 (s, 5, Ph), 6.58 (d, 1, *J* = 6 Hz, CHSH), 8.25 (d, 1, *J* = 6 Hz, CHSH), 9.90 (s, 9, GeMe<sub>3</sub>).

Quenching with an HCl-H<sub>2</sub>O-THF solution gave 19 parts  $\alpha$ -mercaptotoluene, 6 parts **1b**, 71 parts **2b**, and 4 parts  $\alpha$ -trimethylgermylthio- $\alpha$ -trimethylgermyltoluene, a species apparently arising from **2b'** during or after quenching:  $n_D^{20}$  1.5482; nmr (CCl<sub>4</sub>, TMS)  $\tau$  2.83 (m, 5, Ph), 6.68 (s, 1, PhCH), 9.76 (s, 9, GeMe<sub>3</sub>), 9.92 (s, 9, GeMe<sub>3</sub>).

*Anal.* Calcd for C<sub>13</sub>H<sub>24</sub>Ge<sub>2</sub>S: C, 43.67; H, 6.77; S, 8.99. Found: C, 45.30; H, 6.68; S, 10.08.

**Rearrangement of Methylthiodimethyl-*tert*-butylsilane (5).** *tert*-Butyllithium solution (11 ml, 13.6 mmol) was added to 2 g (12.4 mmol) of **5** in 11 ml of THF at -78°. After 16 hr at -40°, aqueous acidification gave, upon work-up, 1.9 g (92%) of an oil consisting of 65 parts recovered **5** and 35 parts dimethyl-*tert*-butylsilylmethanethiol (**6**): ir (neat) 2560 (SH) and 1250 cm<sup>-1</sup> (SiMe<sub>2</sub>); 100 MHz nmr (CCl<sub>4</sub>, TMS),  $\tau$  8.34 (d, 2, *J* = 7 Hz, CH<sub>2</sub>-SH), 8.88 (t, 1, *J* = 7 Hz, CH<sub>2</sub>SH), 9.11 (s, 9, Si-*t*-Bu), 9.96 (s, 6, SiMe<sub>2</sub>); mass spectrum (70 eV) *m/e* (rel intensity) M<sup>+</sup> 162 (3), M - 15 147 (2), M - 57 105 (100).

**Rearrangements with Lithium Diisopropylamide.** *n*-Butyllithium solution (15 ml, 24 mmol) was added to 2.4 g (24 mmol) of diisopropylamine in 15 ml THF at -78°. **1a** (3.1 g, 16 mmol) was then added. After holding the solution at 0° for 5 min, glacial acetic acid in THF was injected at -78°. The salts were washed out with water, and the solvent was evaporated from the organic layer. The resultant oil, analyzed by glc, consisted of 15 parts **3a** and 85 parts **2a**. Before water washing, the analysis had been 7 parts **1a**, 8 parts **3a**, and 85 parts **2a**.

**Thermal Rearrangement of  $\alpha$ -Mercapto- $\alpha$ -trimethylsilyltoluene (2a).** **2a** was heated neat, under nitrogen, to 195° in a sealed tube (Decalin vapor bath). Samples were analyzed at regular time intervals by glc using a QF-1 column held at 140°, without appreciable isomerization occurring in the chromatography. After 48 min, 91% conversion to benzylthiotrimethylsilane (**1a**) had occurred. For each sample, the logarithm of the concentration of **2a** was plotted against the time the sample was heated. A straight line resulted,  $t_{1/2}$  = 12 min.

One tube in which was sealed a 50-50 mixture of **1a** and benzonitrile and a second tube in which was sealed a 50-50 mixture of **2a** and xylene were heated together at 195°. After 15 min glc analysis

showed 50% conversion of **2a** to **1a** in the first tube, 53% in the second.

$\alpha$ -Mercapto- $\alpha$ -trimethylgermyltoluene (**2b**) was isomerized in the same fashion to **1b**. Rearrangement was first order in **2b**,  $t_{1/2} = 3$  min.

#### Radical Rearrangement of $\alpha$ -Mercapto- $\alpha$ -trimethylsilyltoluene

(**2a**). **2a** (250 mg, 1.3 mmol) was heated to 100° in heptane in the presence of azobisisobutyronitrile (17 mg, 0.2 mmol). Glc analysis after 37 min showed 92% isomerization to benzylthiotrimethylsilane (**1a**) had occurred.

**2b** was isomerized in the same fashion to **1b**, 96% isomerization occurring after 10 min.

## New Anionic Rearrangements. XIX. Stereochemistry of the Alkoxysilane to Silylcarbinol Anion Rearrangement<sup>1-3</sup>

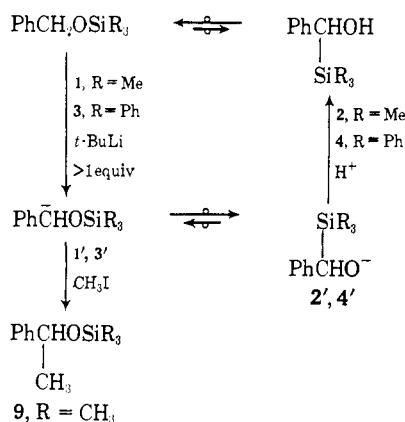
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**Abstract:** Metalation of *S*-(+)-benzyl- $\alpha$ -*d*-oxytrimethylsilane (*S*-(+)-**5**) with excess *tert*-butyllithium at -50° occurs rapidly at benzyl carbon with a hydrogen/deuterium isotope ratio  $k_H/k_D = 24 \pm 4$ , the highest value ever reported for a metalation reaction. The resulting carbanion undergoes a rapid intramolecular rearrangement to the oxyanion of *S*-(-)- $\alpha$ -hydroxy- $\alpha$ -trimethylsilyl- $\alpha$ -*d*-toluene (*S*-(-)-**6**). Acidification of the anion solution yields the silylcarbinol *S*-(-)-**6**. Rearrangement occurs stereospecifically with 99% inversion at benzyl carbon, showing that silicon migrates very rapidly to the benzyl carbanion center. The anion of *S*-(-)-**6** racemizes slowly at 25° and reacts with methyl iodide to give the unrearranged totally racemic derivative 1-phenyl-1-trimethylsiloxyethane-1-*d*. Racemization of the anion thus appears to occur by equilibration with the carbanion isomer. *S*-(+)-Benzyl- $\alpha$ -*d*-oxytrimethylgermane and *S*-(+)-benzyl- $\alpha$ -*d*-oxytriphenylsilane also rearrange with inversion of configuration at carbon. Analysis of *S*-(-)-**6** for isotopic and optical purity was performed by nmr spectroscopy in the presence of tris(3-heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III). This chiral shift reagent shows simultaneously both an isotope effect and an enantiomeric effect in the magnitude of resonance displacement.

We have reported<sup>5</sup> that benzyloxytrimethylsilane, upon metalation at the benzyl carbon atom with excess *tert*-butyllithium at -78°, undergoes a rapid intramolecular isomerization to the anion of the silylcarbinol  $\alpha$ -hydroxy- $\alpha$ -trimethylsilyltoluene (**1**  $\rightarrow$  **2'**, Scheme I). Whereas protonation of the anion **2'** gives

Scheme I



the silylcarbinol **2**, methylation of the anion with methyl iodide at 25° slowly gives **9**, which is derived from the unrearranged carbanion **1'**. The alkoxysilane

to silylcarbinol anion rearrangement is formally analogous to the classical Wittig rearrangement of metalated benzyl ethers to anions of secondary alcohols.<sup>6</sup> However, its mechanism appears to be more closely related to that of the Brook rearrangement, in which silylcarbinols rearrange to alkoxysilanes under base catalysis.<sup>7,8</sup>

We sought to use some of the same techniques to study the anion rearrangement as have been used to study the Brook rearrangement, hoping thereby to make an explicit comparison of their mechanisms. Recently Biernbaum and Mosher,<sup>9</sup> in an elegant study, proved that the catalytic rearrangement proceeds stereoselectively with 90–100% inversion of configuration at benzyl carbon, not retention as had been previously supposed<sup>11</sup> (Scheme II). It seemed possible to use this system in reverse in order to elucidate the stereochemistry of the anion rearrangement.

#### Rearrangement of *S*-(+)-Benzyl- $\alpha$ -*d*-oxytrimethylsilane

Because of its ease of metalation, *S*-(+)-benzyl- $\alpha$ -*d*-oxytrimethylsilane (*S*-(+)-**5**) was more convenient to study initially than the triphenylsilyl analog *S*-(+)-**7**. The *S* configuration has been assigned to (+)-benzyl-

(6) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

(7) A. G. Brook, G. E. Legrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967).

(8) A. G. Brook, *Accounts Chem. Res.*, in press.

(9) M. S. Biernbaum and H. S. Mosher, *J. Amer. Chem. Soc.*, **93**, 6221 (1971). Inversion at carbon was also recently observed in an independent study by A. G. Brook.<sup>10</sup>

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(11) A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

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(2) Previous paper in this series: A. Wright and R. West, *J. Amer. Chem. Soc.*, **96**, 3222 (1974).

(3) Presented in part at the Third International Symposium on Organosilicon Chemistry, Madison, Wis., August 1972.

(4) Procter and Gamble Fellow, 1972–1973.

(5) A. Wright and R. West, *J. Amer. Chem. Soc.*, **96**, 3214 (1974).